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<p>(54) Title: <b>NON-CROSSLINKED POLYETHENE</b></p> <p>(57) Abstract</p> <p>The invention relates to non-crosslinked polyethylene which value of the normalised difference between its storage modulus G' and its loss modulus G'', determined by dynamic rheological measurement, is continuously below 0,5 under frequencies from 0,01 to 100 rad/s and at the temperature 190 °C. Preferably, said difference is essentially constant under said frequencies. Such polyethenes are preferably prepared by using metallocene catalysts, most preferably based on rac-ethylene bis(3-tri-isopropylsiloxy)indenyl zirconium dichloride or rac-ethylene bis(3-tert-butylidimethylsiloxy)indenyl zirconium dichloride.</p>			

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## Non-crosslinked polyethene

### Field of the invention

5 The object of the invention is a non-crosslinked polyethene with novel rheological properties. The invention also relates to the polymerisation of said non-crosslinked polyethene.

### Background of the invention

10 The narrow molar mass distribution that is characteristic of metallocene polymers is associated with desirable mechanical properties. However, these materials show, in comparison to low density polyethene (PE-LD), unfavourable behaviour in processing, such as melt fracture due to the small shear sensitivity and melt elasticity.

15 Improvement of the processability can be reached by either broadening the molar mass distribution or by introducing long chain branching to the polymer. Of these two alternatives, increasing the degree of long chain branching while maintaining the narrow molar mass and comonomer distribution is more desirable. The pseudoplasticity (shear thinning) and melt elasticity of these polymers are improved, while maintaining the desired mechanical properties.

20 The patent application EP 676 421 describes a metallocene catalyst and polymerisation conditions leading to polyolefins having at least 0.01 long chain branches per 1000 carbon atoms along the polymer backbone and a breadth of molar mass distribution ( $M_w/M_n$ ) greater than 2,5. A particularly preferred metallocene complex is a C<sub>2</sub>-bridged bis(indenyl)zirconium dichloride.

25 The polymerisation described in EP 676 421 is preferably carried out in gas-phase in the presence of a cocatalyst such as methyl aluminoxane. The polymers according to this publication show increased shear thinning compared to other single site catalysts. Their shear thinning behaviour is conventional, i.e. the polymers show increased shear rate dependency of the viscosity. The processing window is, however, still rather narrow which can cause problems like melt fracture, extruder high back pressure, bubble instability in blow film processes and sagging in blow molding.

30 Further, single site polymer gives narrow molecular weight distribution which limits extrudability of those polymers.

The processing window can now be broadened by using the novel non-crosslinked polyethene of the present invention. This non-crosslinked polyethene having novel rheological properties shows throughout the shear rate range, already at very low shear rates, both high elasticity and increased shear rate dependency of the viscosity.

5

### Description of the invention

The non crosslinked polyethene according to the invention is such that the value of the normalised difference between its storage modulus  $G'$  and its loss modulus  $G''$ , determined by dynamic rheological measurement, is continuously below 0,5 under 10 frequencies from 0,01 to 100 rad/s and at the temperature 190°C. The curves  $G'$  and  $G''$  are thus essentially parallel in said frequency range.

Such rheological behaviour, which does not occur in prior non crosslinked polyethenes, means that the polymers are very elastic at low shear rates. Thus the processing of the polymer is facilitated since also the shear thinning (or sensitivity) is increased and the range of optimal process parameters is widened without modifying the molar mass.

15 The non crosslinked polyethene according to the invention has preferably been polymerised with a catalyst system comprising a metallocene complex. Said metallocene complex is a metallocene having a sandwich bonding ligand comprising a sandwich bonding moiety having an unsaturated 5-membered ring or having a 6-membered ring fused to an unsaturated 5-membered ring which moiety is covalently 20 substituted by an organic group via a heteroatom.

25 Preferably, said moiety comprises an indenyl, dihydroindenyl or tetrahydroindenyl ring system. Said moiety is also preferably substituted by a silyloxy or germyloxy group.

Most preferably said metallocene complex is rac-ethylene bis(3-tri-isopropylsiloxy)indenyl zirconium dichloride or rac-ethylene bis(3-tert-butylidimethylsiloxy)indenyl zirconium dichloride.

30 Further, said metallocene complex is preferably supported, the support being silica, alumina and/or magnesium dichloride.

According to a preferred embodiment of the invention, the polymerisation is carried out in a slurry process, in which a  $C_3$ - $C_8$  inert hydrocarbon e.g. propane, isobutane,

pentane, heptane, hexane, toluene or any other aliphatic or aromatic solvent is used as polymerisation medium.

The reaction temperature is preferably from 60 to 110°C, more preferably from 75 to 100°C.

5 The polymerisation conditions are preferably such that the ethene partial pressure is from 0,25 to 40,0 bar, preferably from 5,0 to 15,0 bar. Hydrogen is optionally used, preferably in an amount from 0,1 to 10 mol, more preferably from 0,5 to 2 mol per 1000 mol of ethene.

10 Comonomer can also be used in the polymerisation and preferably the comonomer is an  $\alpha$ -olefin, preferably a C<sub>4</sub>-C<sub>8</sub>  $\alpha$ -olefin. The amount of comonomer is such that the comonomer content of the final product is from 1,0 to 10,0 wt-%, preferably from 3,0 to 10,0 wt-%, most preferably from 5,0 to 8,0 wt-%.

15 When a cocatalyst is needed, an alkyl aluminoxane is preferably used, and most preferably said alkyl aluminoxane is methyl aluminoxane, hexaisobutyl aluminoxane and/or tetraisobutyl aluminoxane. The amount of alkyl aluminoxane used is such that Al/Metal-ratio is from 50 to 2500, preferably from 100 to 1500.

Consequently, the non crosslinked polyethene according to the invention has the desirable mechanical properties characteristic of metallocene polymers associated to good processability due to long chain branching.

## 20 Experimental

### Polymerisations

The polymerisations were performed in a 3 L semiflow stainless steel autoclave reactor equipped with a paddle stirrer and an external glycol jacket for temperature control. The reactor was dried and degassed thoroughly prior to use.

25 Molar mass (M<sub>w</sub> in g/mol) and molar mass distribution (MMD) as M<sub>w</sub>/M<sub>n</sub>, measured by gel permeation chromatography (GPC), and rheological properties at 190 °C of the polymers of the examples are given in Table 1.

### Example 1

1800 mL of dry pentane, 0,25  $\mu$ mol catalyst rac-ethylene bis(3-tri-30 isopropylsiloxy)indenyl zirconium dichloride and 0,0538 mL 30 wt-% methyl alu-

minoxane (MAO) in toluene were added to the reactor. The ratio Al/Zr was 1000. 0,2 bar of hydrogen (vessel size 512,25 mL) was fed batchwise with ethene to the reactor. Ethene flow was adjusted so that the ethene partial pressure in the reactor was 5,0 bar.

5 The polymerisation was allowed to run for 30 minutes at 80°C and the reactor was let to cool after releasing the pressure. The medium was evaporated off the polymer. 89,7 g of polymer was recovered (Figure 1).

#### Example 2

10 The procedure was identical to that in example 1, but the polymerisation time was 15 minutes. 64,6 g of polymer was recovered (Figure 2).

#### Example 3

15 The procedure was identical to that in example 1, but now also 25 mL 1-hexene was added to the reactor batchwise with ethene and the polymerisation time was 15 minutes. 82,5 g of copolymer was recovered, which comonomer content was 6,7 wt-% (Figure 3).

#### Example 4

1800 mL of dry pentane, 0,3  $\mu$ mol of catalyst rac-ethylene bis(3-tert-butylmethoxysiloxyl)indenyl zirconium dichloride and 0,136 mL 30 wt-% methyl aluminoxane (MAO) in toluene were added to the reactor. 25 mL of 1-hexene was added batchwise to the reactor with ethene. Ethene flow was adjusted so that the ethene partial pressure in the reactor was 2,5 bar.

The polymerisation was allowed to run for 30 minutes at 80°C. The reactor was let to cool after releasing the pressure and the medium was evaporated off the polymer. 17 g of polymer was recovered, which comonomer content was 7,2 w-% (Figure 4).

25 Example 5

1200 ml of dry pentane and 0,0538 ml 30 wt-% methyl aluminoxane (MAO) in toluene were added to the reactor.

30 Heterogeneous catalyst was prepared by mixing 34,2 mg of rac-ethylene bis(3-triisopropylsiloxy)indenyl zirconium dichloride with 1,98 mL of 30 wt-% methyl aluminoxane and further diluting the mixture with 0,55 mL of toluene. After 1 hour

reaction time 1,48 mL of the complex solution obtained was slowly impregnated on activated silica (0,987 g Sylopol 55SJ, activated at 600°C). Impregnation time was 1 hour after which the catalyst was dried by nitrogen purging.

196,3 mg of said heterogeneous catalyst was added to the reactor. The ration Al/Zr 5 was 208. Ethene flow was adjusted so that the ethene partial pressure in the reactor was 5,0 bar. The polymerisation was allowed to run for 60 minutes at 80 °C. The reactor was let to cool after realeasing the pressure and the medium was evaporated off the polymer. 104 g of polymer was recovered (Figure 5).

Comparative examples 6-8 are examples of polymers catalysed with metallocenes 10 and containing some long chain branching.

#### **Comparative example 6**

Using the same procedure as in example 1, but 0,5 µmol of catalyst rac-ethylene (bis)indenyl zirconium dichloride, 0,11 mL 30 wt-% methyl aluminoxane (MAO) in toluene and 25 ml 1-hexene were used.

15 The polymerisation was allowed to run for 60 minutes at 80°C. 109 g of polymer was recovered (Figure 6).

#### **Comparative example 7**

Using the same procedure as in example 5, but 1,0 µmol of catalyst rac-ethylene (bis)indenyl zirconium dichloride and 0,22 mL 30 wt-% methyl aluminoxane 20 (MAO) in toluene were used.

The polymerisation was allowed to run for 60 minutes at 80°C. 74,3 g of polymer was recovered, its comonomer content was 5,5 wt-% (Figure 7).

#### **Comparative example 8**

1800 mL of dry pentane, 0,5 µmol of catalyst rac-ethylene (bis)-4, 5, 6, 7-25 tetrahydroindenyl zirconium dichloride and 0,11 mL 30 wt-% methyl aluminoxane (MAO) in toluene were added to the reactor. 0,2 bar of hydrogen (vessel size 512,25 mL) and 50 mL of 1-hexene were both added batchwise to the reactor with ethene. Ethene partial pressure was 10 bar.

The polymerisation was allowed to run for 60 minutes at 80°C. 155,6 g of polymer 30 was recovered, which comonomer content was 2,5 wt-% (Figure 8).

Comparative examples 9 and 10 are examples of linear polymers catalysed with metallocenes.

#### Comparative example 9

5 The same procedure as in example 1 was used, but 1800 mL of dry pentane and 297,8 mg of heterogeneous catalyst based on di-(n-butylcyclopentadienyl)zirconium dichloride prepared above were used. The Al/Zr ratio was 200.

The polymerisation was allowed to run for 60 minutes at 80°C and 205,4 g of polymer was recovered (Figure 9).

#### Comparative example 10

10 1800 mL of dry toluene, 0,5  $\mu$ mol of catalyst di-(n-butylcyclopentadienyl)zirconium dichloride and 0,0538 mL 30 wt-% methyl aluminoxane (MAO) in toluene were added to the reactor. Al/Zr ratio was 1000. 45 mL of 1-hexene was added to the reactor batchwise with ethene. Ethene flow was adjusted so that the ethene partial pressure in the reactor was 5,0 bar.

15 The polymerisation was allowed to run for 60 minutes at 80°C and the reactor was let to cool after releasing the pressure. The polymer was then precipitated with ethanol, washed and dried in vacuum. 60,0 g of polymer was recovered which co-monomer content was 1,2 wt-% (Figure 10).

#### Rheological measurements

20 The viscoelastic parameters, loss modulus  $G'(\omega)$  and storage modulus  $G''(\omega)$  were determined on a Rheometric Scientific stress controlled dynamic rheometer SR-500 with the parallel plates geometry under the following conditions:

25 - polymer sample appropriately stabilised prior to testing (e.g. containing 2000 ppm of a thermal/oxidative stabiliser, e.g. Irganox B 215 commercially available from Ciba-Geigy),

- frequency range from 0,01 or 0,02 to 100 rad/s,

- temperatures 170°C, 190°C and 210°C and

- the strain amplitude was operator-chosen for best signal in linear viscoelastic region.

The data treatment of the results includes:

- an appropriate software (e.g. Rheometrics RSI Orchestrator software) used to shift the moduli curves along the frequency axis with compensation for the effect of temperature on melt density to construct the master curves and to determine the shift factor  $a_T$ ,
- 5 - fitting the resultant shift factors  $a_T$  to Arrhenius equation for evaluation of flow activation energy  $E_a$  from  $a_T=\exp(E_a/RT)$  and
- displaying the master curve data, the elastic modulus  $G'(\omega)$  and the viscous modulus  $G''(\omega)$ ,versus frequency  $\omega$ .

10 The samples tested were those prepared in examples 1-10 as well as three reference materials, that were commercial low density polyethene (PE-LD, Figure 11), high density polyethene (PE-HD, (Figure 12) and linear low density polyethene (PE-LLD, (Figure 13). The results are summarised in Table 1 (Tables 1a and 1b): melt flow rate at weight 21 kg (MFR<sub>21</sub>, in g/10 min), molar mass  $M_w$ , molar mass distribution MMD, complex viscosity  $\eta^*$  at 0,02 rad/s and 190 °C (in Pa.s),  $\omega_{\text{cross-over}}$ , that is the value of the modulus  $G$  ( $=G'=G''$ ) at which the curves of  $G'$  and  $G''$  cross each other, polydispersity index PI, that is the value of  $10^5/G$  in the cross-over point, branching index  $g'$  and flow activation energy  $E_a$  (in kJ/mol). The branching index  $g'$  values were calculated as  $g' = \eta(\text{branched}) / \eta(\text{linear})$ , where  $\eta(\text{branched})$  and  $\eta(\text{linear})$  were measured by GPC-on-line viscometry.

15

20

The PE-LD reference sample was characterised by high molar mass, broad molar mass distribution and a flow activation energy of 50 kJ/mol, typical for low density polyethene. The PE-LLD sample was a conventional Ziegler-Natta catalysed film grade linear low density polyethene,  $M_w$  80 000 g/mol and MMD 4,0, yielding 33 kJ/mol for flow activation energy. The PE-HD sample was a chromium catalysed high density polyethene with few or no long chain branches, characterised by high molar mass ( $M_w$  300 000 g/mol) and broad MMD (15). The flow activation energy of this material was 31 kJ/mol.

25

Table 1. Polymer properties

Example	MFR <sup>21</sup> (g/10 min)	M <sub>w</sub> (kg/mol)	MMD	η <sup>*</sup> (Pa.s)	ω <sub>cross-over</sub> (rad/s)	PI (10 <sup>5</sup> /G <sub>cross-over</sub> )	g'	E <sub>a</sub> (kJ/mol)
1	26,9	116	4,8	31000	n.c.	-	0,94	n.a.
2	33,3	117	5,5	32300	n.c.	-	n.m.	n.a.
3	11,0	132	3,7	373000	0,04	13,1	0,80	n.a.
4	12,4	113	2,9	369000	0,03	18,9	n.m.	n.a.
5	3,7	191	5,8	172000	0,04	16,8	n.m.	n.a.
6	21,7	102	2,7	68500	4,4	4,1	0,70	n.a.
7	32,4	112	3,2	20800	n.c.	-	0,76	48
8	39,6	117	3,6	13600	n.c.	-	0,95	33
9	24,1	110	2,3	5810	n.c.	-	0,99	30
10	n.m.	300	2,2	150000	9,4	0,3	n.m.	27
PE-HD	n.m.	n.m.	n.m.	193000	17,3	4,1	n.m.	30
PE-LD	n.m.	n.m.	n.m.	14000	1,1	3,7	n.m.	55
PE-LLD	n.m.	n.m.	n.m.	5600	n.c.	-	n.m.	33

n.c. no modulus cross-over in the measured frequency range

n.a. not applicable

n.m. not measured

The frequency dependency of the dynamic moduli of the samples are shown in figures 1-13. Figures 1-5 show the corresponding curves for samples prepared in examples 1-4, according to the invention. Figures 6-10 show the curves for the comparative samples prepared in examples 6-10 and figures 11-13 show the curves for the reference materials PE-LD, PE-HD and PE-LLD.

In figures 1 and 2 the curve representing the storage modulus  $G'(\omega)$  is parallel to that of loss modulus  $G''(\omega)$  over the whole measured frequency region, four decades (0,01-100 rad/s). In figures 3-5, the two curves are essentially parallel over the frequency region from 0,3 or 0,4 to 100 rad/s. In figures 6-10 the storage modulus  $G'(\omega)$  is not parallel to the loss modulus  $G''(\omega)$  over any part of the frequency region studied. Such is the case also in figures 11-13.

In Table 2 is disclosed calculated values for tan delta ( $G''/G'$ ) and the normalised difference

$$(G''-G')/\sqrt{(G''^2+G'^2)}$$

15 in the whole frequency range obtained from data of  $G''$  and  $G'$ . As can be seen from this data, the examples of the invention fulfill the conditions

- I. no moduli cross-over in the range of 0,05-100 rad/s, and
- B. tan delta values are below 2,1 and the normalised difference is below 0,5 in the whole frequency range (0,02-100 rad/s).

Table 2. Normalised difference (nd) and calculated tan delta (td) versus frequency

Example	Freq. (rad/s)	1		2		3		4		5		6		7	
		nd	td	nd	td										
0,02	0,47	2,10	0,46	2,03	0,08	0,12	0,02	1,03	0,06	0,92	0,62	2,87	0,70	3,63	
0,03	0,44	1,97	0,42	1,89	0,03	1,04	0,01	0,98	0,02	0,98	0,55	2,46	0,64	3,08	
0,05	0,40	1,82	0,37	1,75	0,02	0,97	0,06	0,92	0,00	1,00	0,48	2,14	0,58	2,64	
0,08	0,36	1,72	0,34	1,65	0,08	0,90	0,11	0,86	0,01	1,02	0,42	1,89	0,52	2,31	
0,13	0,33	1,64	0,31	1,57	0,12	0,84	0,15	0,81	0,03	1,04	0,35	1,70	0,46	2,06	
0,2	0,31	1,59	0,28	1,52	0,16	0,80	0,19	0,77	0,04	1,06	0,29	1,54	0,41	1,86	
0,32	0,31	1,57	0,27	1,49	0,19	0,76	0,22	0,73	0,05	1,08	0,24	1,41	0,35	1,70	
0,5	0,30	1,56	0,27	1,47	0,22	0,73	0,25	0,69	0,06	1,09	0,18	1,29	0,30	1,56	
0,8	0,30	1,56	0,27	1,47	0,24	0,71	0,28	0,66	0,06	1,09	0,13	1,20	0,25	1,44	
1,26	0,32	1,60	0,28	1,50	0,24	0,70	0,30	0,65	0,06	1,08	0,08	1,12	0,21	1,35	
2	0,34	1,65	0,30	1,55	0,24	0,70	0,31	0,64	0,05	1,08	0,05	1,07	0,17	1,28	
3,17	0,35	1,70	0,32	1,59	0,24	0,71	0,31	0,63	0,04	1,06	0,01	1,02	0,14	1,22	
5,02	0,36	1,72	0,32	1,61	0,23	0,71	0,30	0,64	0,02	1,03	0,01	0,99	0,12	1,18	
7,96	0,36	1,71	0,32	1,61	0,22	0,73	0,29	0,65	0,01	0,99	0,03	0,96	0,10	1,15	
12,62	0,34	1,67	0,31	1,59	0,21	0,73	0,27	0,67	0,04	0,94	0,04	0,95	0,09	1,13	
20	0,32	1,61	0,29	1,54	0,21	0,74	0,25	0,69	0,08	0,89	0,05	0,94	0,08	1,12	
31,7	0,28	1,51	0,26	1,46	0,21	0,74	0,24	0,71	0,13	0,83	0,05	0,94	0,08	1,12	
50,24	0,23	1,39	0,21	1,35	0,22	0,72	0,22	0,73	0,18	0,77	0,05	0,93	0,07	1,10	
79,62	0,17	1,27	0,16	1,25	0,24	0,70	0,22	0,73	0,23	0,71	0,05	0,93	0,05	1,08	
100	0,13	1,21	0,12	1,19	0,26	0,69	0,22	0,73	0,26	0,68	0,06	0,92	0,04	1,06	

Table 2. (continued)

Example Freq. (rad/s)	8			9			10			11			12			13		
	nd	td	td	nd	td	td	nd	td	td	nd	td	td	nd	td	td	nd	td	
0,02	0,80	5,30	0,98	50,89	0,84	6,67	0,90	10,65	0,25	1,44	0,93	0,93	14,01					
0,03	0,77	4,71	0,98	45,63	0,83	6,25	0,86	7,68	0,23	1,39	0,91	0,91	11,19					
0,05	0,74	4,17	0,97	35,63	0,82	5,83	0,81	5,75	0,20	1,34	0,89	0,89	9,41					
0,08	0,71	3,77	0,96	28,67	0,80	5,41	0,76	4,45	0,18	1,29	0,87	0,87	8,12					
0,13	0,68	3,43	0,96	23,72	0,78	4,93	0,69	3,55	0,15	1,24	0,85	0,85	7,27					
0,2	0,65	3,15	0,95	19,07	0,75	4,37	0,62	2,92	0,12	1,19	0,84	0,84	6,53					
0,32	0,62	2,92	0,93	15,57	0,71	3,81	0,55	2,48	0,10	1,15	0,82	0,82	6,00					
0,5	0,59	2,72	0,92	12,66	0,66	3,23	0,48	2,13	0,07	1,10	0,80	0,80	5,46					
0,8	0,56	2,83	0,90	10,34	0,59	2,68	0,41	1,85	0,03	1,05	0,78	0,78	4,88					
1,26	0,53	2,37	0,87	8,41	0,50	2,22	0,33	1,64	0,00	1,01	0,75	0,75	4,33					
2	0,51	2,25	0,85	6,85	0,40	1,84	0,27	1,48	0,02	0,97	0,72	0,72	3,92					
3,17	0,48	2,11	0,81	5,56	0,29	1,53	0,20	1,34	0,05	0,93	0,68	0,68	3,41					
5,02	0,45	1,99	0,76	4,53	0,17	1,28	0,14	1,22	0,09	0,89	0,63	0,63	2,99					
7,96	0,41	1,88	0,70	3,69	0,05	1,07	0,09	1,13	0,12	0,85	0,58	0,58	2,62					
12,62	0,37	1,75	0,64	3,02	0,08	0,90	0,03	1,05	0,15	0,81	0,52	0,52	2,30					
20	0,33	1,62	0,56	2,49	0,19	0,76	0,01	0,98	0,19	0,77	0,45	0,45	2,03					
31,7	0,28	1,50	0,47	2,07	0,30	0,64	0,06	0,92	0,22	0,72	0,38	0,38	1,78					
50,24	0,23	1,38	0,37	1,73	0,40	0,55	0,10	0,86	0,26	0,69	0,31	0,31	1,57					
79,62	0,16	1,26	0,26	1,46	0,48	0,47	0,14	0,82	0,30	0,65	0,23	0,23	1,39					
100	0,13	1,20	0,20	1,34	0,52	0,43	0,16	0,80	0,33	0,61	0,15	0,15	1,24					

**Claims**

1. Non crosslinked polyethene, characterised in that the value of the normalised difference between its storage modulus  $G'$  and its loss modulus  $G''$ , determined by dynamic rheological measurement, is continuously below 0,5 under frequencies from 0,01 to 100 rad/s and at the temperature 190°C.  
5
2. Non crosslinked polyethene according to claim 1, characterised in that the absolute value of the difference between its storage modulus  $G'$  and its loss modulus  $G''$ , determined by dynamic rheological measurement, is continuously higher than 0 under frequencies from 0,1 to 100 rad/s and at the temperature 190°C.
- 10 3. Non crosslinked polyethene according to claim 2, characterised in that said absolute value of the difference between its storage modulus  $G'$  and its loss modulus  $G''$  is essentially constant.
- 15 4. Non crosslinked polyethene according to any preceding claim, characterised in that it has been prepared by selecting for the polymerisation a catalyst system comprising a metallocene complex.
- 20 5. Non crosslinked polyethene according to claim 4, characterised in that said metallocene complex is a metallocene having a sandwich bonding ligand comprising a sandwich bonding moiety having an unsaturated 5-membered ring or having a 6-membered ring fused to an unsaturated 5-membered ring which moiety is covalently substituted by an organic group via a heteroatom.
6. Non crosslinked polyethene according to claim 5, characterised in that said moiety comprises an indenyl, dihydroindenyl or tetrahydroindenyl ring system.
7. Non crosslinked polyethene according to claim 5 or 6, characterised in that said moiety is substituted by a silyloxy or germyloxy group.
- 25 8. Non crosslinked polyethene according to claim 7, characterised in that said metallocene complex is rac-ethylene bis(3-tri-isopropylsiloxy)indenyl zirconium dichloride.
9. Non crosslinked polyethene according to claim 7, characterised in that said metallocene complex is rac-ethylene bis(3-tert-butyldimethylsiloxy)indenyl zirconium dichloride.  
30

10. Non crosslinked polyethene according to any of claims 4-9, characterised in that said metallocene complex is supported.
11. Non crosslinked polyethene according to claim 10, characterised in that said metallocene complex is supported on silica, alumina and/or magnesium dichloride.
- 5 12. Non crosslinked polyethene according to any of claims 4-11, characterised in that said polymerisation is carried out in a slurry process.
- 10 13. Non crosslinked polyethene according to claim 12, characterised in that a C<sub>3</sub>-C<sub>8</sub> inert hydrocarbon e.g. propane, isobutane, pentane, heptane, hexane, toluene or any other aliphatic or aromatic solvent is used as medium in said slurry polymerisation.
14. Non crosslinked polyethene according to claim 12 or 13, characterised in that said slurry polymerisation is carried out at a temperature from 60 to 110°C, preferably at a temperature from 75 to 100°C.
15. Non crosslinked polyethene according to any of claims 12-14, characterised in that the ethene partial pressure in the polymerisation is from 0,25 to 40,0 bar, preferably from 2,0 to 15,0 bar, most preferably from 5,0 to 7,0 bar.
16. Non crosslinked polyethene according to any of claims 12-15, characterised in that hydrogen is optionally used in said slurry polymerisation.
17. Non crosslinked polyethene according to any of claims 12-16, characterised in that comonomer is used in said slurry polymerisation.
- 20 18. Non crosslinked polyethene according to claim 17, characterised in that said comonomer is an α-olefin, preferably a C<sub>4</sub>-C<sub>8</sub> α-olefin.
19. Non crosslinked polyethene according to claim 17 or 18 characterised in that the amount of comonomer is such that the comonomer content of the final product is from 1,0 to 10,0 wt-%, preferably from 3,0 to 10,0 wt-%, most preferably from 5,0 to 8,0 wt-%.
- 25 20. Non crosslinked polyethene according to any of claims 12-19, characterised in that an alkyl aluminoxane is used as cocatalyst in said slurry polymerisation.

21. Non crosslinked polyethene according to claim 20, characterised in that said alkyl aluminoxane is methyl aluminoxane, hexaisobutyl aluminoxane and/or tetra-isobutyl aluminoxane.

22. Non crosslinked polyethene according to claim 20 or 21, characterised in that the amount of alkyl aluminoxane used is such that Al/Metal-ratio is from 50 to 5

2500, preferably from 100 to 1500.

23. Slurry polymerisation process for the preparation of non crosslinked polyethene, which value of the normalised difference between its storage modulus  $G'$  and its loss modulus  $G''$ , determined by dynamic rheological measurement, is continuously below 0,5 under frequencies from 0,01 to 100 rad/s and at temperature 10

190 °C, wherein the process parameters are chosen from the following:

- (i) reaction medium is an inert C<sub>3</sub>-C<sub>8</sub> hydrocarbon or toluene,
- (ii) catalyst is based on a metallocene complex, and is optionally supported,
- (iii) reaction temperature is 60 - 110 °C,
- 15 (iv) ethene partial pressure is 0,25 - 40,0 bar,
- (v) hydrogen is optionally used,
- (vi) comonomer is optionally used,
- (vii) cocatalyst is an alkyl aluminoxane, and Al/Metal-ratio is 50-2500.

Fig. 1

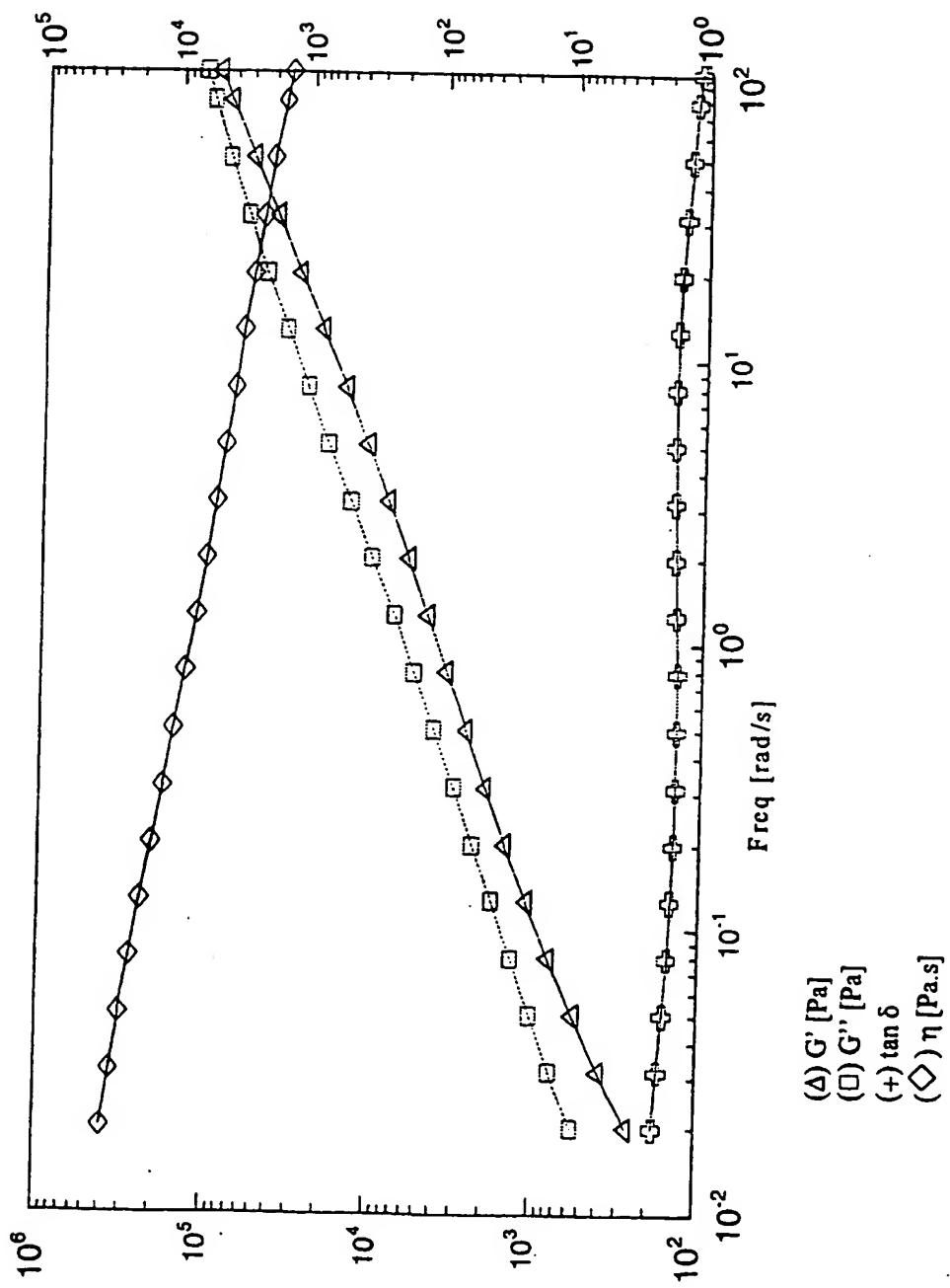
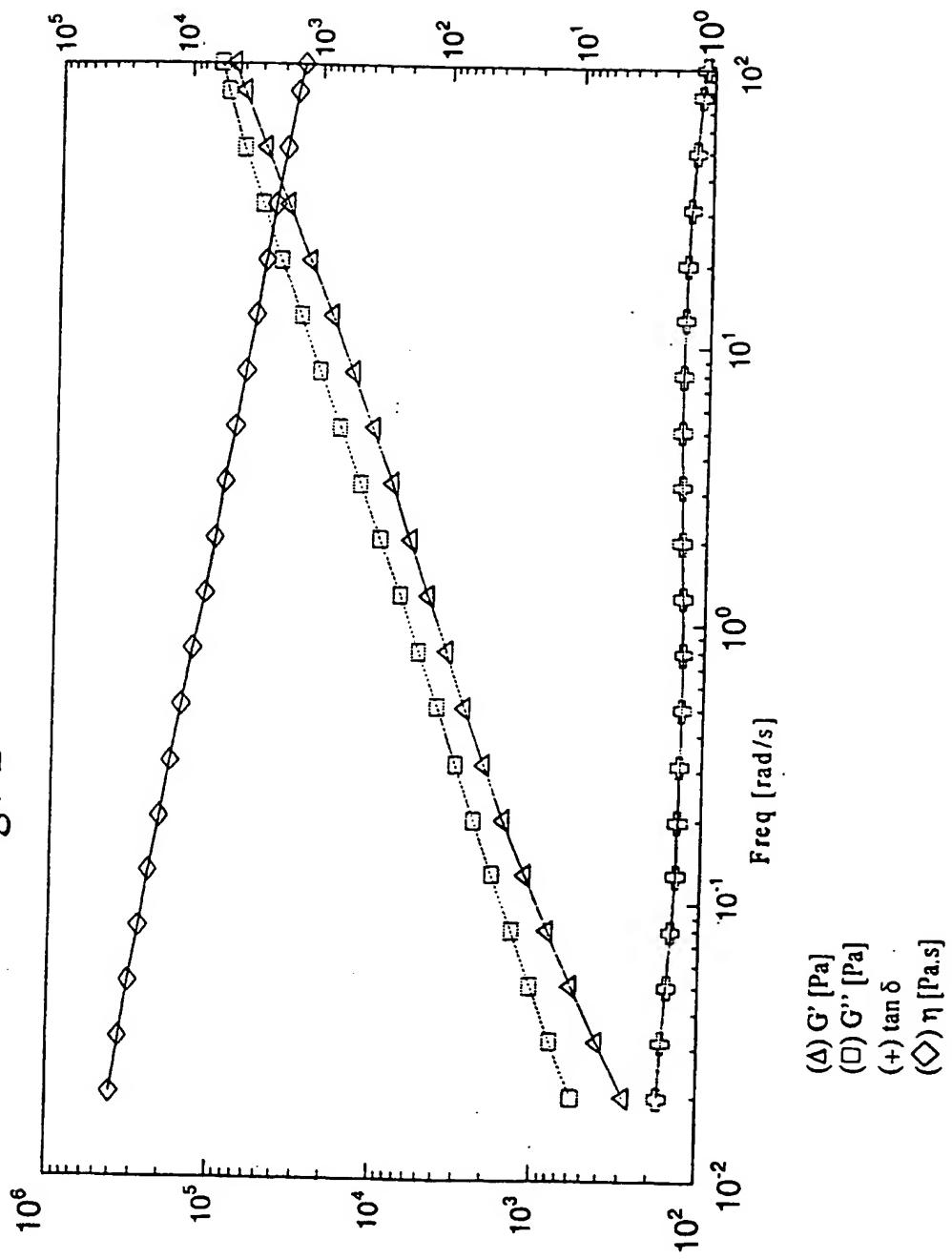


Fig. 2



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Fig. 3

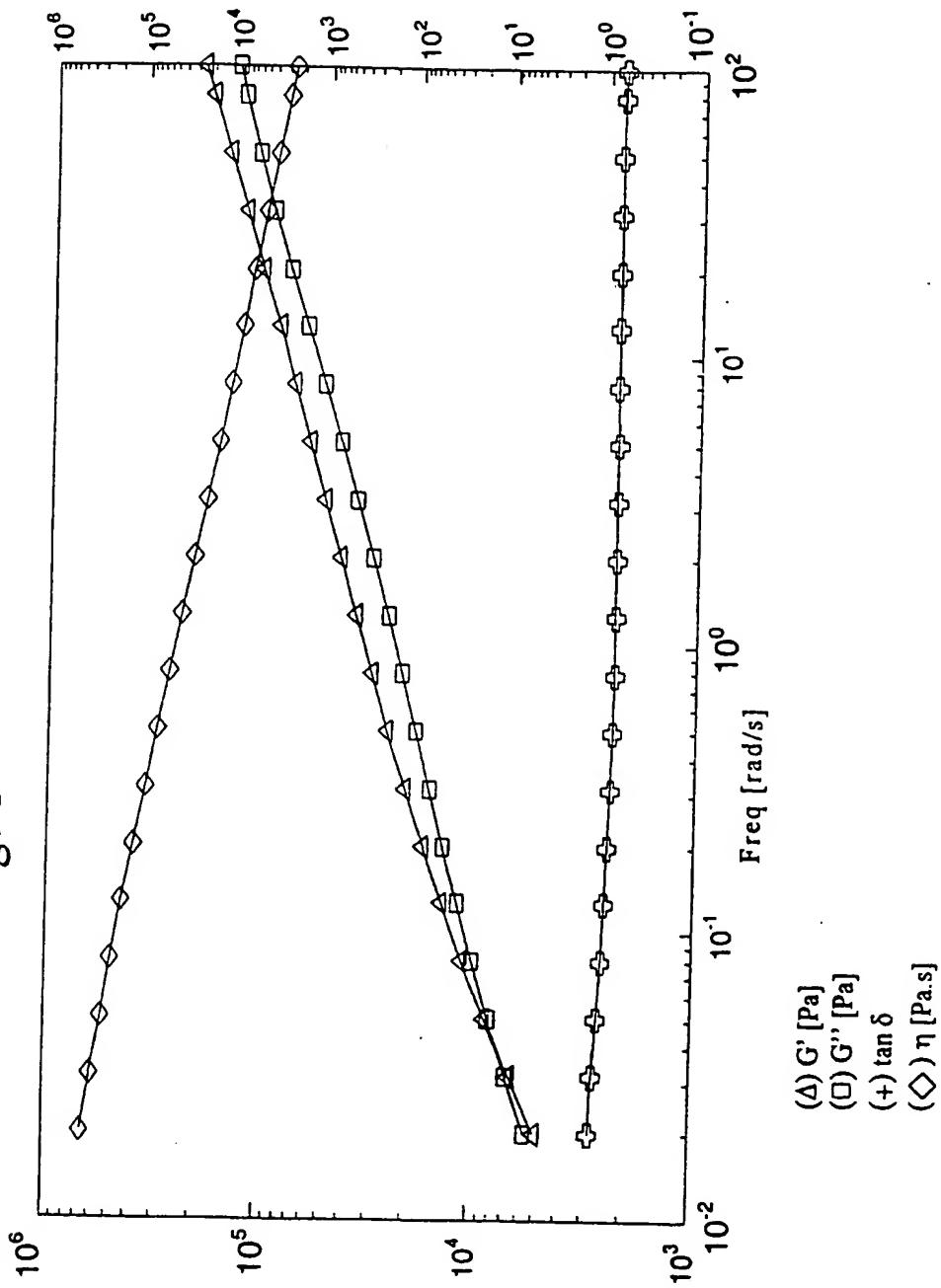


Fig. 4

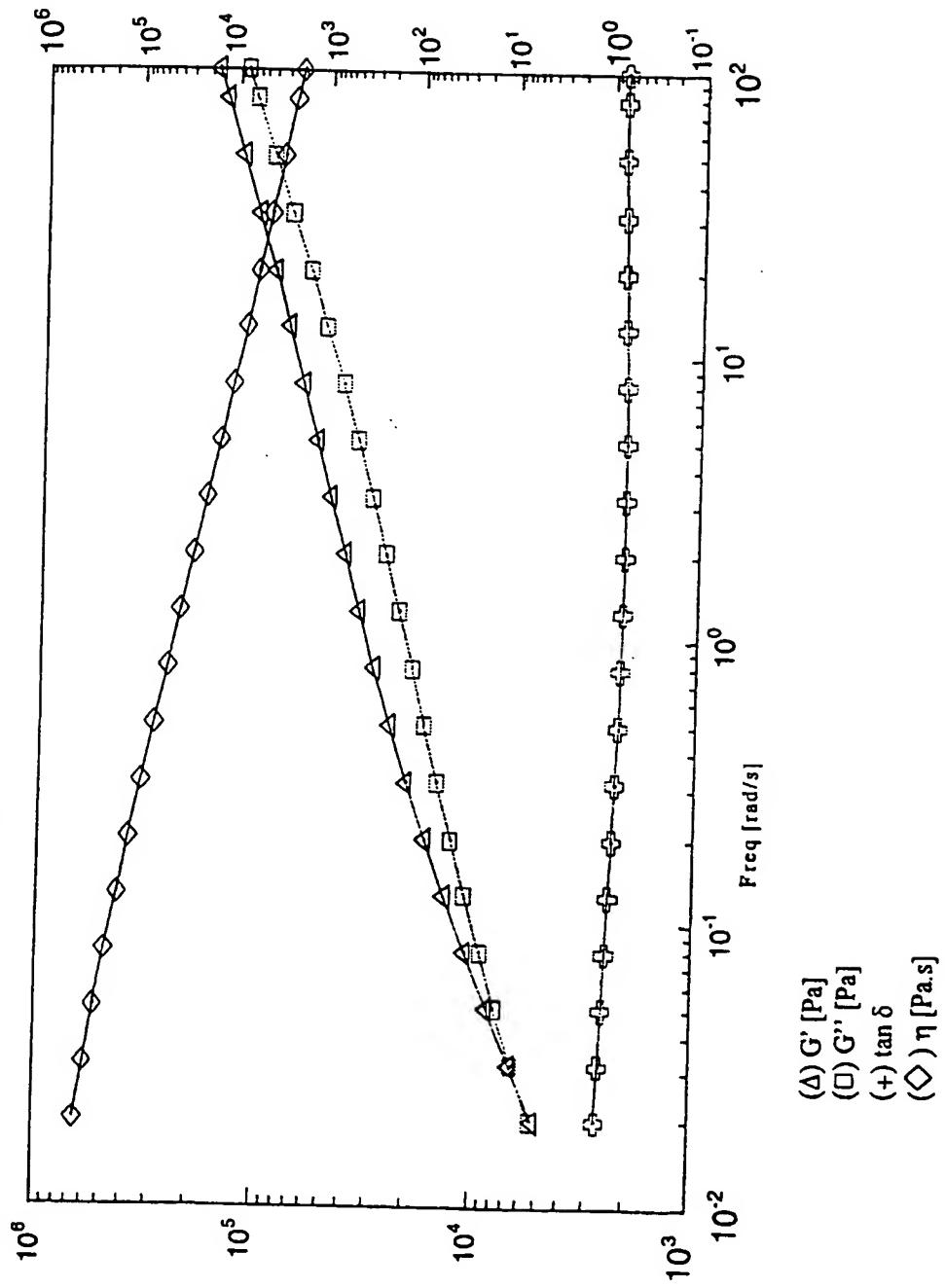
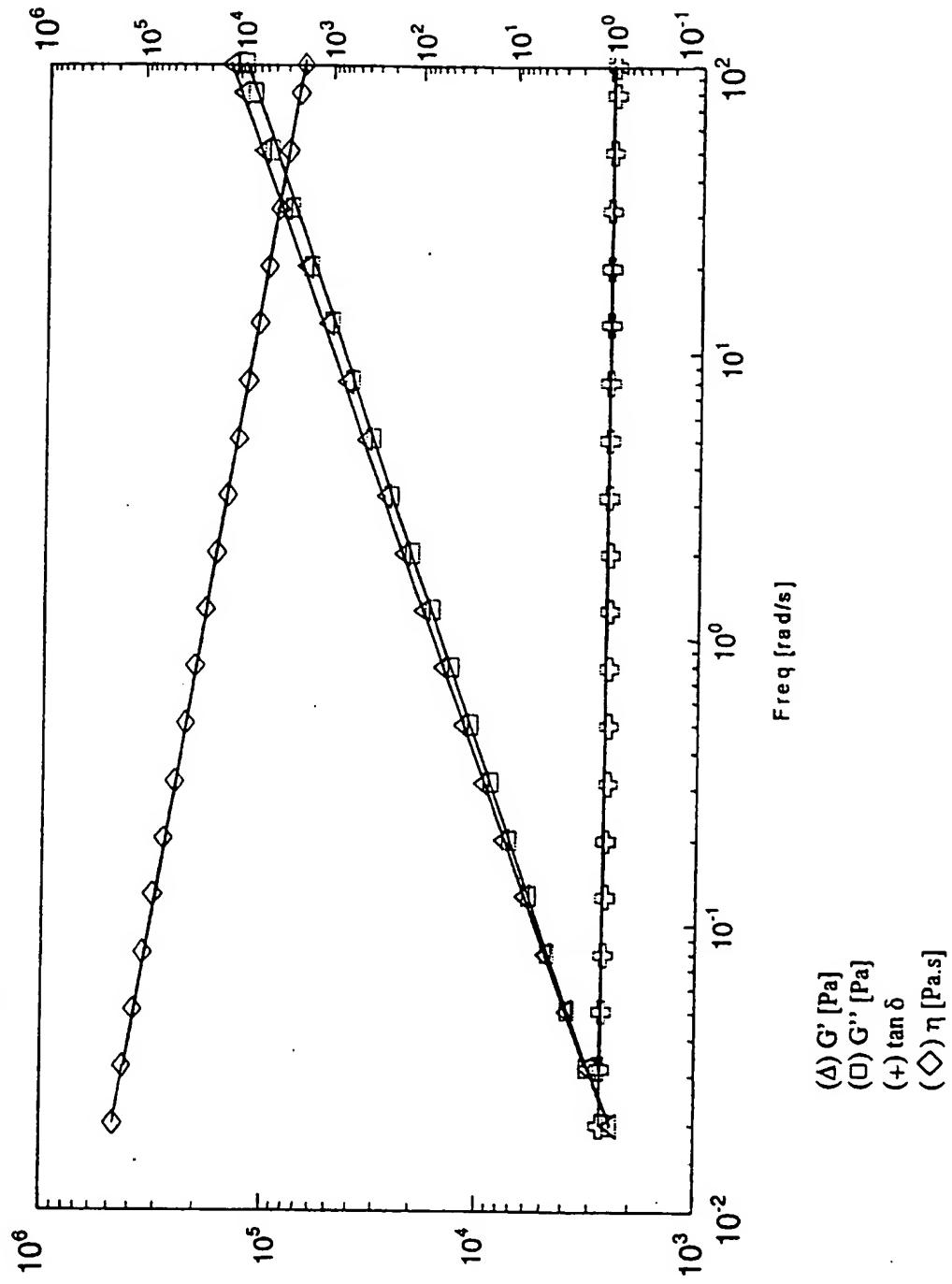


Fig. 5



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Fig. 6

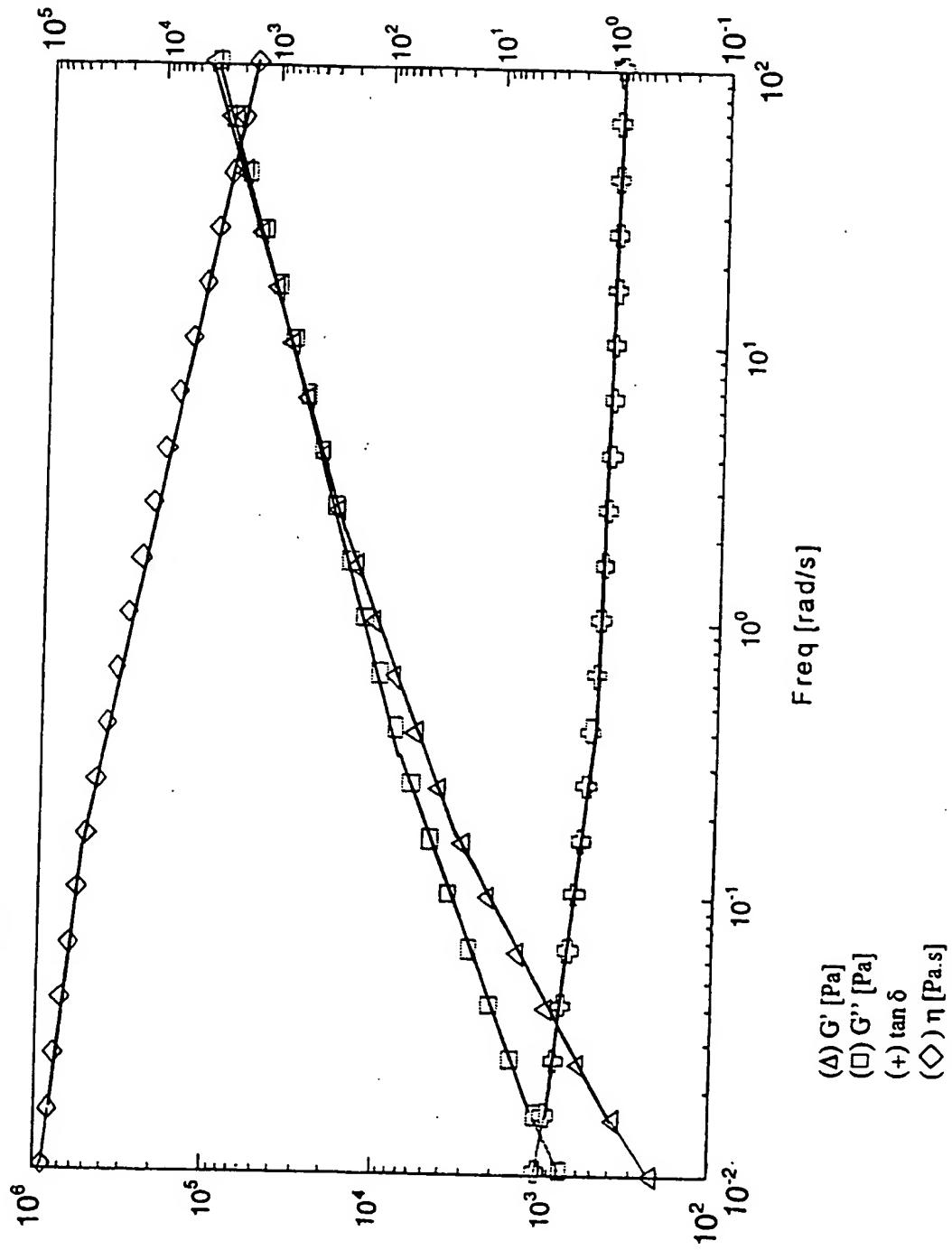
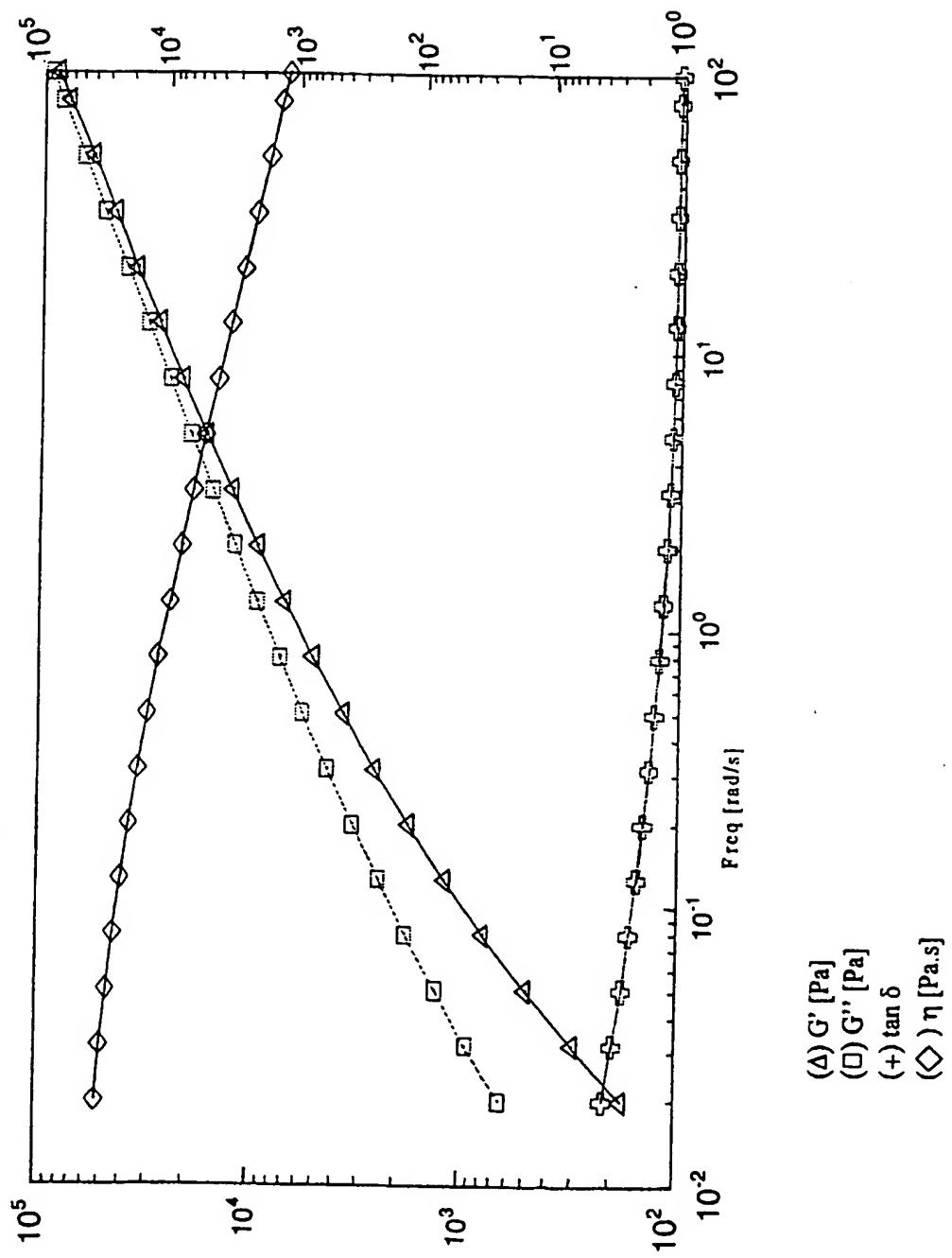


Fig. 7



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Fig. 8

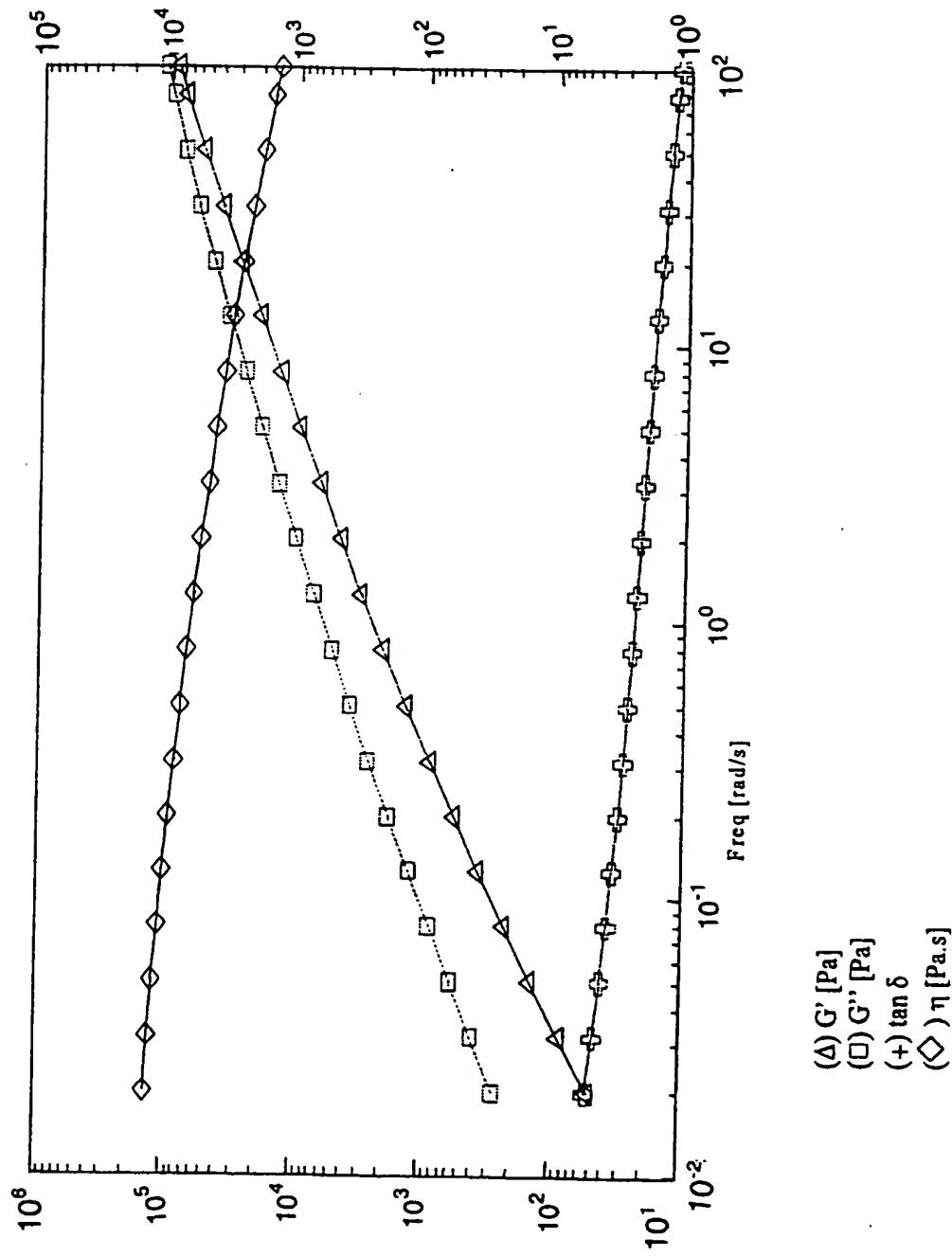
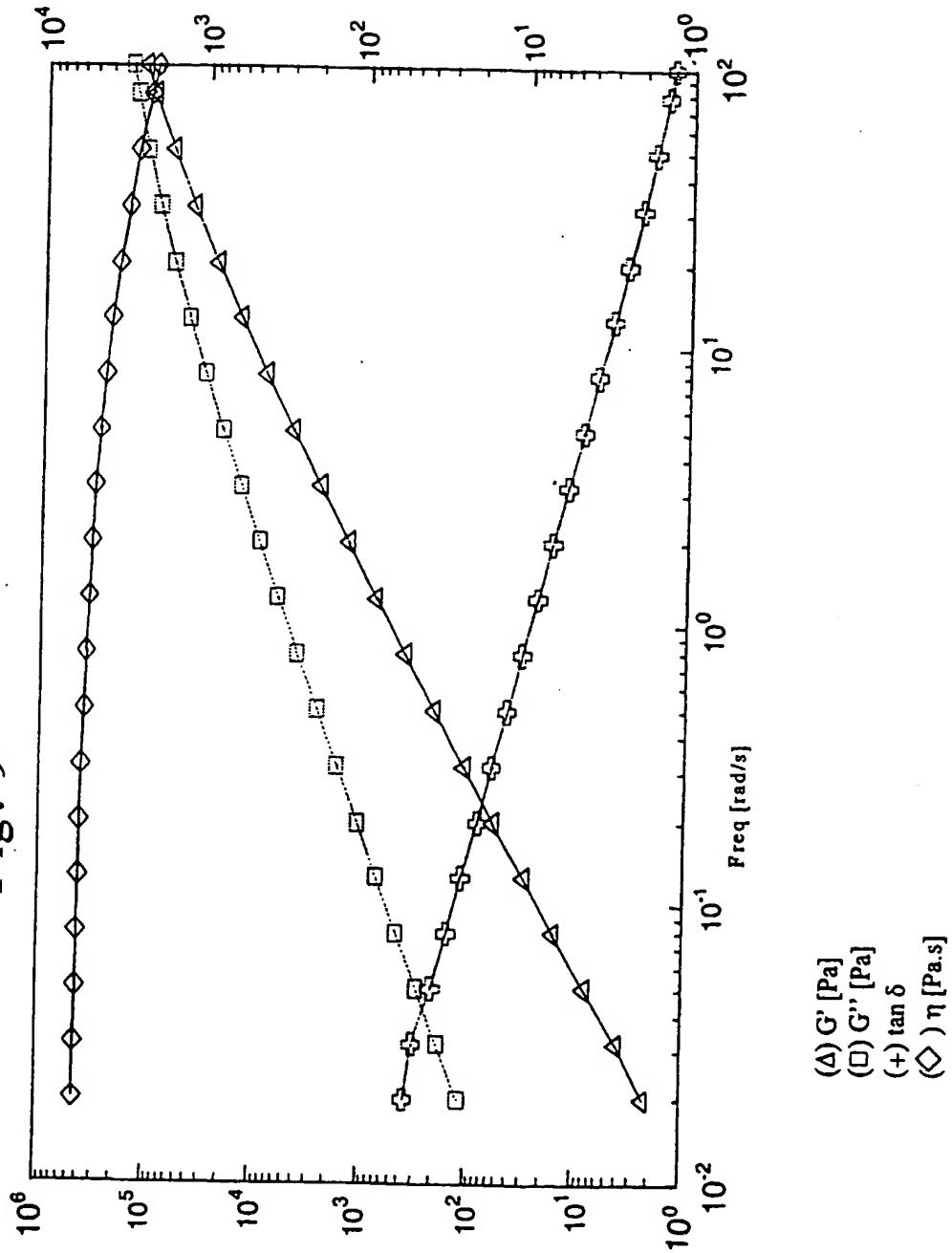
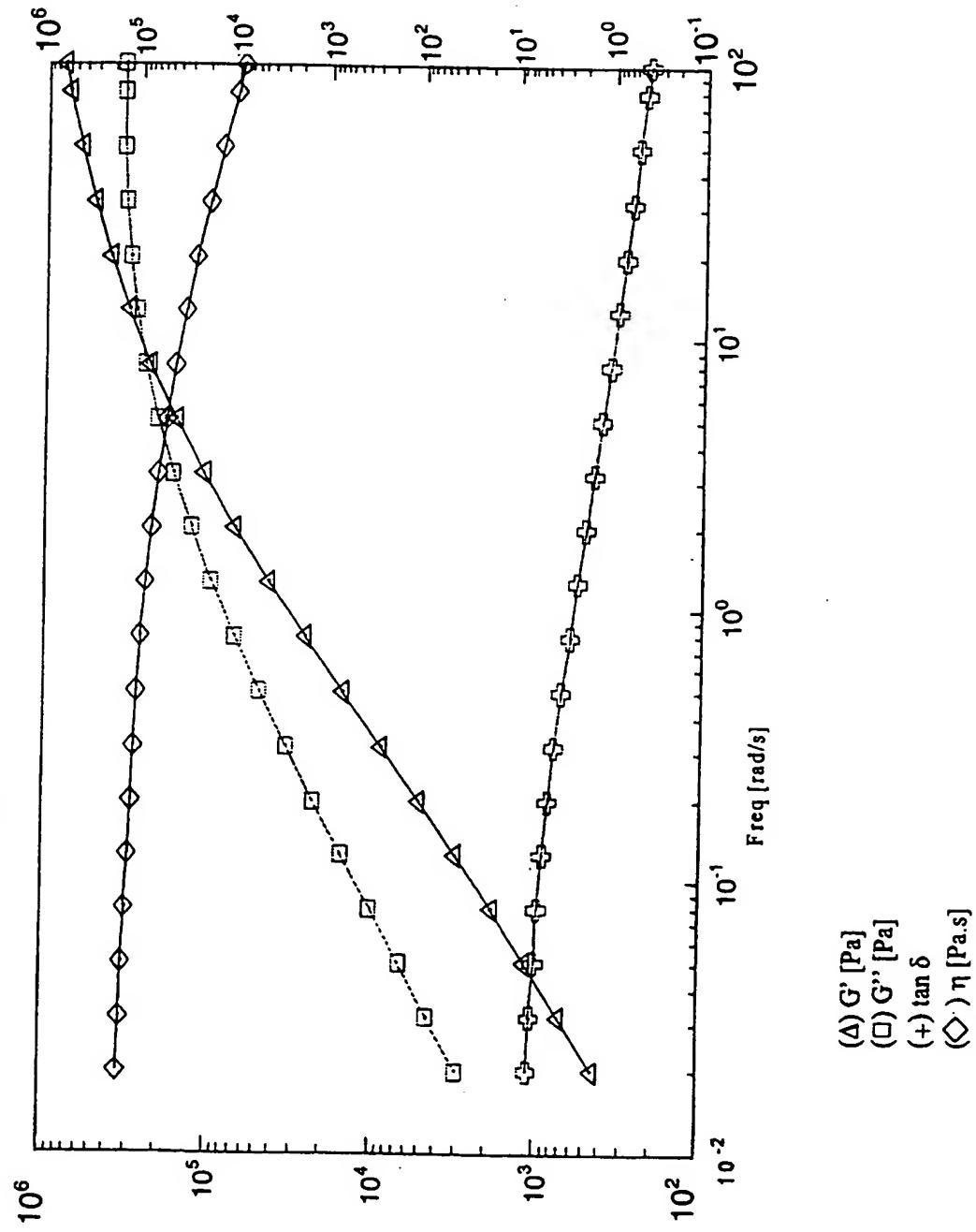


Fig. 9



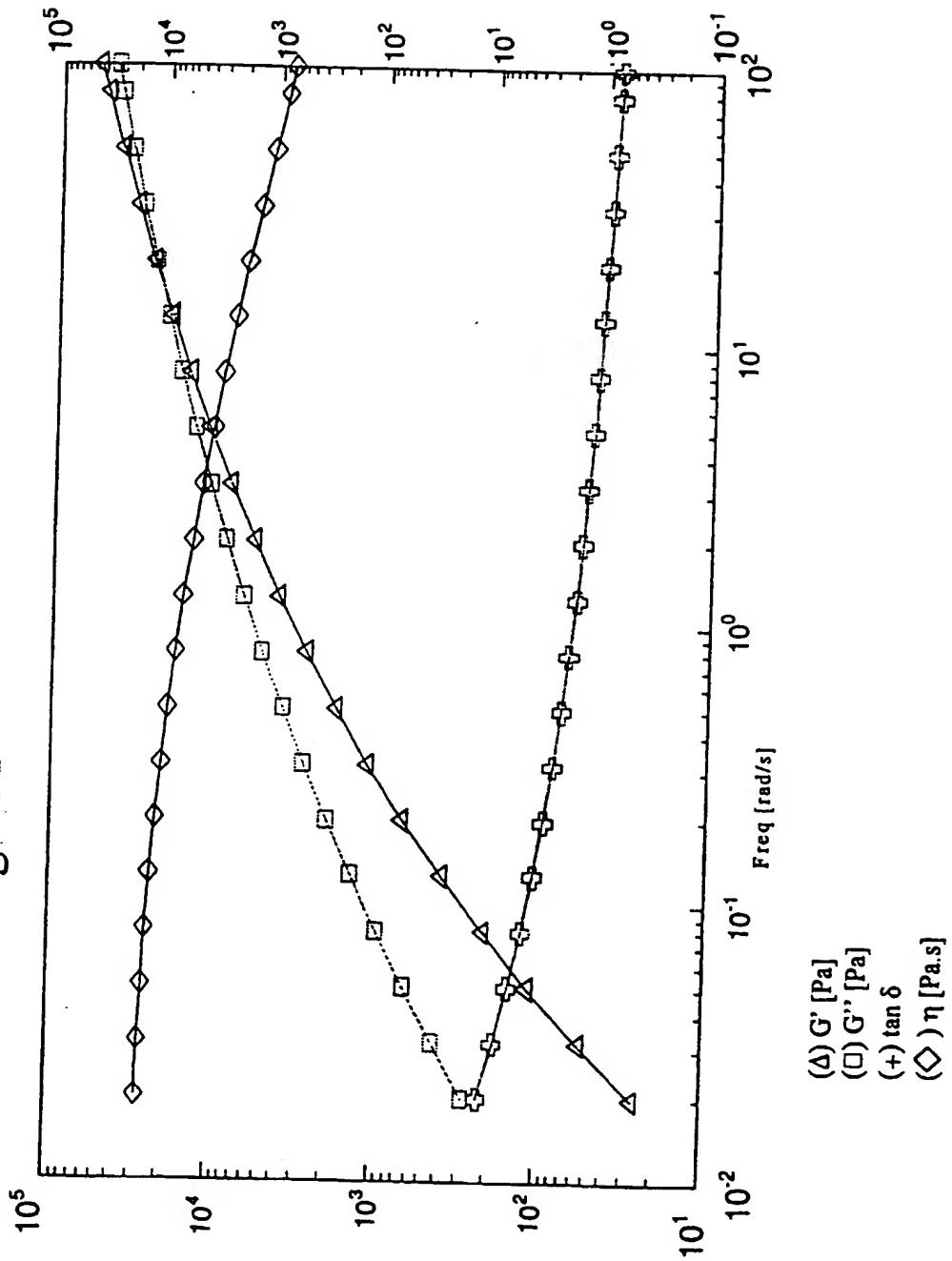
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Fig. 10



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Fig. 11



**SUBSTITUTE SHEET (Rule 26)**  
**SUBSTITUTE SHEET (RULE 26)**

12/13

Fig.12

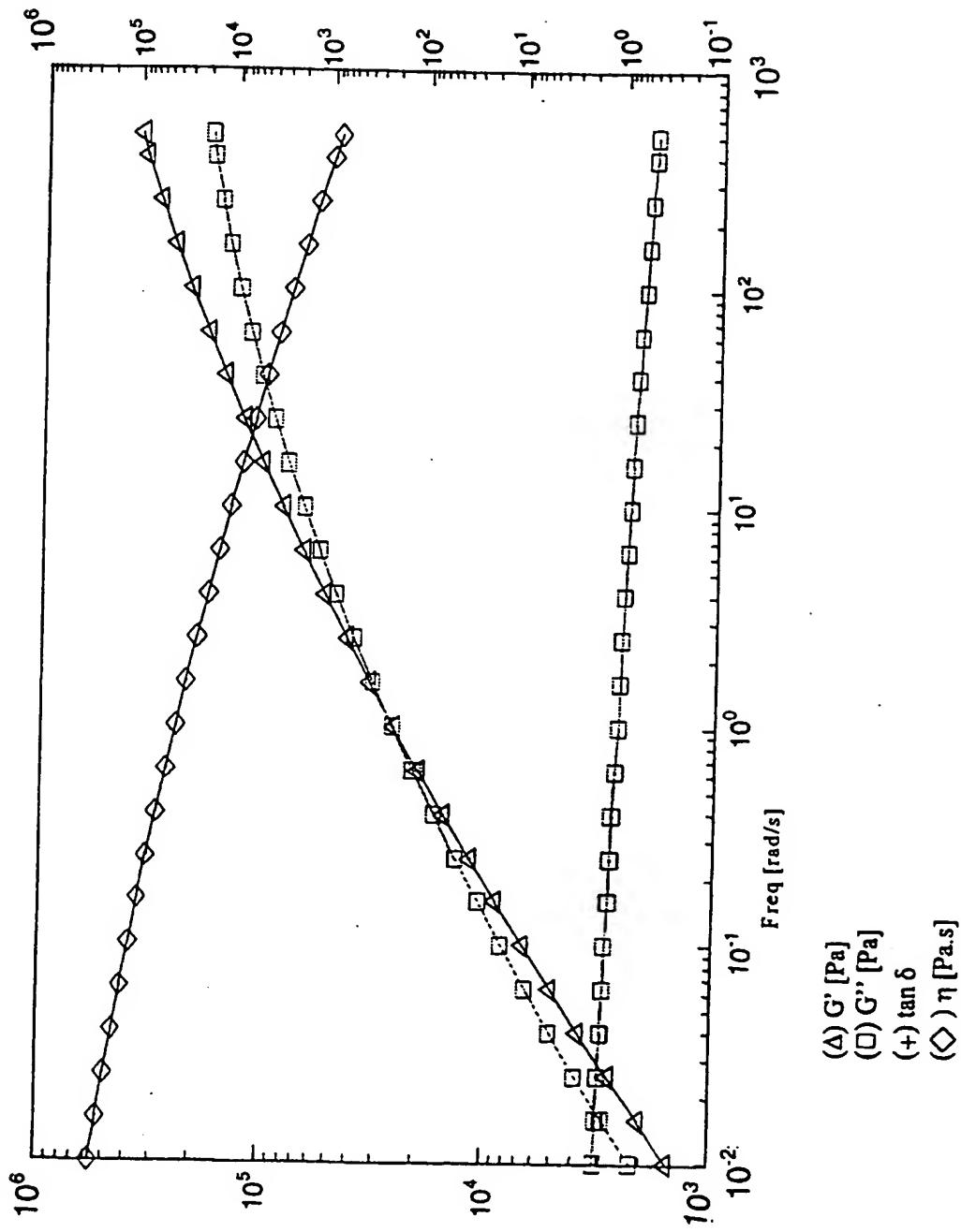
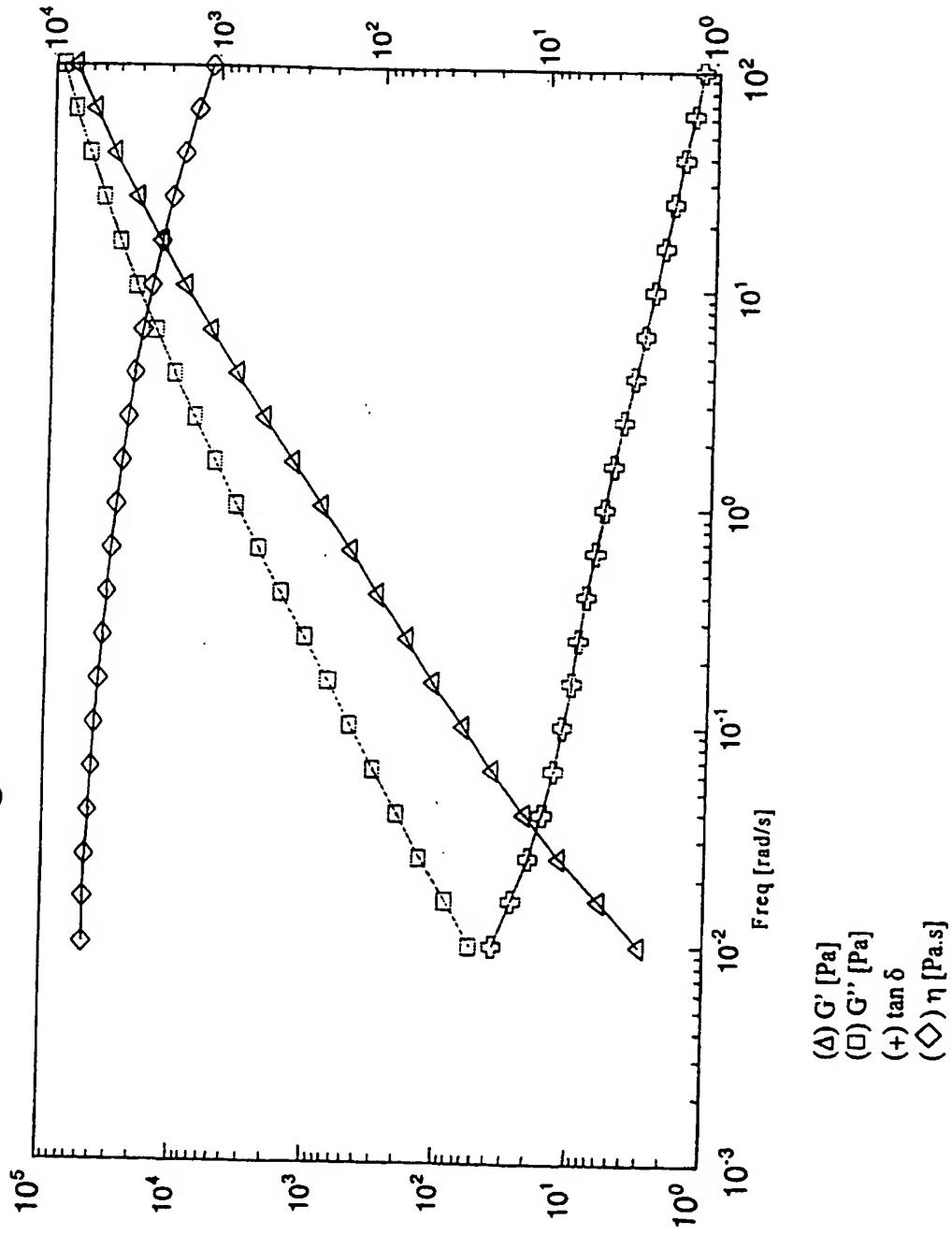


Fig. 13



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(51) International Patent Classification<sup>7</sup>: C08F 10/02 (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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— With international search report.

(88) Date of publication of the international search report: 1 February 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/64952 A3

(54) Title: NON-CROSSLINKED POLYETHENE

(57) Abstract: The invention relates to non-crosslinked polyethylene which value of the normalised difference between its storage modulus G' and its loss modulus G'', determined by dynamic rheological measurement, is continuously below 0.5 under frequencies from 0.01 to 100 rad/s and at the temperature 190 °C. Preferably, said difference is essentially constant under said frequencies. Such polyethenes are preferably prepared by using metallocene catalysts, most preferably based on rac-ethylene bis(3-tert-butylidimethylsiloxy)indenyl zirconium dichloride or rac-ethylene bis(3-tert-butylidimethylsiloxy)indenyl zirconium dichloride.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI 00/00366

## A. CLASSIFICATION OF SUBJECT MATTER

## IPC7: C08F 10/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

## IPC7: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9744371 A1 (THE DOW CHEMICAL COMPANY), 27 November 1997 (27.11.97), page 5, line 9 - line 19; page 19, line 20 - line 36; page 39, line 15 - line 23, page 53, line 26 - line 32; abstract; claims 30-32 --	1-6
X	EP 0729978 A1 (PHILLIPS PETROLEUM COMPANY), 4 Sept 1996 (04.09.96), page 8, line 1 - line 3 --	1-4
X	WO 9607680 A1 (THE DOW CHEMICAL COMPANY), 14 March 1996 (14.03.96), page 3, line 30 - line 31; page 4, line 3 - line 22, abstract, claims --	1-4

Further documents are listed in the continuation of Box C.

See patent family annex.

- \* Special categories of cited documents
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search  
31 August 2000

Date of mailing of the international search report

03.11.2000

Name and mailing address of the International Searching Authority  
European Patent Office P.B. 5818 Patentlaan 2  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00366

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9729138 A1 (EXXON CHEMICAL PATENTS INC.), 14 August 1997 (14.08.97), page 1, line 4 - line 35; page 5, line 13 - line 30; page 13, line 25 - line 29, claims --	1-23
A	EP 0743324 A2 (UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION), 20 November 1996 (20.11.96) --	1-23
A	EP 0676421 A1 (BP CHEMICALS LIMITED), 11 October 1995 (11.10.95) -- -----	1-23

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/FI00/00366**

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: **1-23 (all in part)** because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
**see next page**
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).:

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI00/00366

Present claims 1 – 23 relate to a polymer defined by reference to the following parameters:

P1: Storage modulus, G'

P2: Loss modulus, G"

The use of these parameters in the present context is considered to lead to lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to use with what is set out in prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to:

*Homo- and copolymers of polyethylene with good processability, increased shear thinning and long chain branching.*

SA 31261

## INTERNATIONAL SEARCH REPORT

Information on patent family members

08/05/00

International application No.

PCT/FI 00/00366

Patent document cited in search report	Publication date		Patent family member(s)		Publication date
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		GB	9417365 D		00/00/00